PARTITIONING OF Pd BETWEEN Fe-S-C AND MANTLE LIQUIDS AT HIGH PRESSURE AND TEMPERATURE: IMPLICATIONS FOR CORE FORMATION.

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Introduction: One of the most elusive geochemical aspects of the early Earth has been explaining the near chondritic relative abundances of the highly siderophile elements (HSE; Au, Re and the platinum group elements) in Earth's primitive upper mantle (PUM). Perhaps they were delivered to the Earth after core formation, by late addition of carbonaceous chondrite material [1-3]. However, the recognition that many moderately siderophile elements can be explained by high pressure and temperature (PT) metal-silicate equilibrium [4], leads to the question whether high PT equilibrium can also explain the HSE concentrations.

Answers to this question have been slowed by experimental difficulties (nugget effect and very low solubilities; [5]). But two different perspectives have emerged from recent studies. One perspective is that D(M/S) for HSE at high PT are not low enough to explain terrestrial mantle depletions of these elements (for Pd and Pt; [6,7]). A second perspective is D(M/S) are reduced substantially at high PT and even low enough to explain terrestrial mantle depletions (for Au and Pt; [8,9]). Issues complicating interpretation of all experiments include use of MgO- and FeO-free silicate melts, and S-free and FeNi metal-free systems. In addition, conclusions for Pt rest on an interpretation that the tiny metallic nuggets plaguing many such experiments, were formed upon quench. There is not agreement on this issue, and the general question of HSE solubility at high PT remains unresolved.

Key to resolution of this problem is the ability to work in nugget-free, uncompromised conditions, and to utilize experimental compositions that approximate those of the early Earth (i.e., peridotitic melts and S- and C-bearing FeNi metallic liquids). In order to address this problem, we have undertaken a new series of experiments with the HSE Pd. Pd was chosen for two reasons. First, it is well understood at low pressures with several studies across a range of temperatures and oxygen fugacities [10,11], silicate melt compositional effects are thought to be small [11], and its behavior in S-bearing systems is well known [12]. Second, the formation of nuggets is not reported down to low fO_2 equivalent to IW-1 [10], making analysis and interpretation more straightforward than other nugget-affected elements. New experiments were conducted at NASA Johnson Space Center, and analyzed for Pd at low concentration levels using LA-ICP-MS at Florida State University (FSU).

Experimental: Experiments were conducted at high pressures using both a non end-loaded piston cylinder apparatus and a multi-anvil module in an 880 ton press. The former has been calibrated using fayalite-ferrosilite equilibria and the melting point of diopside [13]. The latter has been calibrated using SiO_2 and Fe_2SiO_4 transitions in a 14/8 assembly with castable octahedra with fins, Re foil furnaces, and type C Re/W thermocouples. Most experiments used MgO capsules containing natural basalt, and Fe-Pd-S-Sb alloy (a few experiments used graphite capsules). The basalt reacts with the MgO to produce more magnesian homogeneous liquids, similar in composition to a komatiite or picrite (Fig. 1). Silicate samples with <20 wt% MgO typically quench to glass (Fig. 2), but those with > 20wt% MgO contain a fine grained matte of silicate quench crystals. Similarly, the metallic liquid quenches to two phases – intergrown Fe-Pd-S-Sb alloy and sulfide. Run products were mounted in epoxy, cut in half along the length of the capsule, and polished for analysis.

Analytical: Run products were analyzed using a Cameca SX100 electron microprobe at NASA-JSC [13] and a New Wave UP213 (213 nm) laser ablation system coupled to a Finnigan Element™ magnetic-sector ICP-MS at the NHMFL at FSU. The peaks [25]Mg, [57]Fe, [59]Co, [60]Ni, [102]Ru, [105]Pd, [106]Pd, [120]Sn, [121]Sb, and [123]Sb were monitored in low resolution at 50 ms/peak. Silicate glasses were analyzed with an 80 µm diameter track scanned at 10 µm/s, and metal blobs were analyzed with 12-15 µm diameter tracks scanned at 5 µm/s, using 10 Hz laser repetition rate and 50% power output. The NIST SRM 1263a steel, and iron meteorites Filomena and Hoba were used as standards.

Results for palladium: Metal/silicate partition coefficients for Pd have been measured for five runs at pressure of 15 kb and temperatures from 1500 to 1700 ˚C. Palladium contents of the silicates and D(Pd) M/S vary between 0.15 and 2.0 ppm, and 73900 and 910, respectively, for the 1500 and 1700 ˚C runs. Because the effects of temperature, oxygen fugacity, melt composition, and metallic liquid S content are known from previous studies, we have derived an equation allowing prediction of D(Pd) M/S [20]:

$$lnD(Pd) = -0.232*lnfO_2 + 7376/T + 8.8*ln(1-Xs) - 0.94(nbo/t) + 7.18 \qquad \text{(equation 1)}$$

This expression will serve as a baseline for comparison of our new high pressure results, and allow isolation of any pressure effect.

To evaluate the results of our high pressure experiments (and those of [6]), the measured values from these studies are normalized to the value calculated for the same T-fO$_2$-X conditions. If there is no change with pressure, the values should be close to 1; if there is a decrease or increase with pressure, they should be <1 or > 1 respectively. The data of [6] show a decrease in D(M/S) for Pd out to 160 kb (Fig. 3). Our new data for entirely different silicate liquids are in agreement with these previous results, suggesting that large compositional differences will not affect D(Pd) substantially. Similarly, the 4 kb and 8 kb results of [15] and [16] also are no different than the D(Pd) M/S calculated for the same T-fO$_2$-X conditions.

A P/T term can be added to equation 1 above to allow prediction of the effect of pressure on D(Pd) M/S. A small and negative value of -20 is consistent with the pressure effect observed by this study and [6,15,16] (dashed line in Figure 3 is a conservative estimate of the pressure effect):

$$lnD(Pd) = -0.232*lnfO_2 + 7376/T – 20*P/T +$$
$$8.8*ln(1-Xs) - 0.94*(nbo/t) + 7.18 \quad (equation\ 2)$$

Use of equation 2 to calculate a D(Pd) M/S at the P-T-fO$_2$-X conditions of 270 kb, 2000 °C, ΔIW = -2, X_S=0.05, and nbo/t = 2.7 (similar to those suggested by [14] for the early Earth), results in a value of 400 (±100), very similar to the value required for core-mantle equilibrium (D = 600). In fact, calculated values for even higher PT, suggested by [17] and [18], result in D(Pd) M/S much lower than 600, thus predicting Pd concentrations far higher than observed in the PUM. High PT conditions may thus be an explanation for suprachondritic Pd/Ir of the PUM [19].

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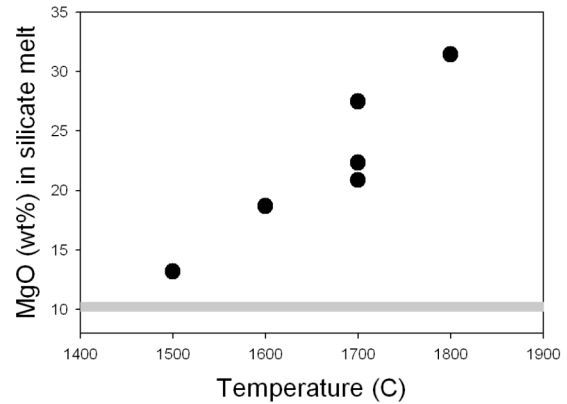

Figure 1: MgO contents of experimental melts equilibrated in an MgO capsule illustrating that MgO-rich liquids are produced at high temperatures (horizontal band is starting MgO content of basalt).
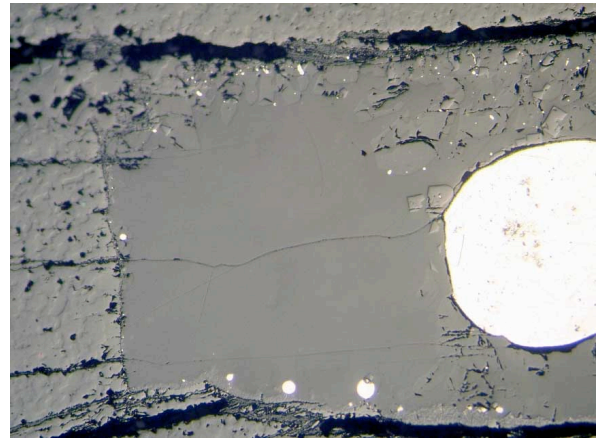

Figure 2: Experimental run product from 15 kb, 1700 °C run with basaltic liquid in MgO capsule. Bright white sphere is quenched liquid metal and grey zone in center is glass.

Figure 3: Pressure effect on D(Pd) M/S showing agreement between our new data and those of [6]; heavy dashed line represents a conservative estimate of the pressure effect of D(Pd) M/S used in equation 2.